

D2

BEST AVAILABLE COPY

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 344 321
A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(21) Application number: 88909129.4

(22) Date of filing: 20.10.88

Data of the international application taken as a basis:

(86) International application number:
PCT/JP88/01067

(87) International publication number:
WO89/03855 (05.05.89 89/10)

(51) Int. Cl.³: **C 08 K 5/34**
C 08 K 5/04, C 08 K 3/00
C 08 L 101/00, C 07 D 211/44
C 07 D 211/58

(30) Priority: 20.10.87 JP 2650/88
13.09.88 JP 227604/88

(43) Date of publication of application:
06.12.89 Bulletin 89/49

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **FERRO CORPORATION**
One Erieview Plaza
Cleveland Ohio 44114(US)

(72) Inventor: **SATO, Yoshinori**
2-7-18, Minamishinosaki
Kazo-shi Saitama 347(JP)

(72) Inventor: **AKAMINE, Hiroshi**
2-7-17, Minamishinosaki
Kazo-shi Saitama 347(JP)

(74) Representative: **Thomas, Roger Tamlyn et al,**
D. Young & Co. 10 Staple Inn
London WC1V 7RD(GB)

(64) SYNTHETIC RESIN COMPOSITION.

(67) A synthetic resin composition which comprises a synthetic resin such as a halogenated resin and 0.01 to 10 parts by weight of a mixture of (a) a compound having at least one piperidyl group, (b) perchloric acid and, if necessary, (c) an inorganic substance other than perchloric acid. This composition shows remarkably excellent resistance against light and heat.

EP 0 344 321 A1

- 1 -

SPECIFICATION

SYNTHETIC RESIN COMPOSITION

Technical field

5 This invention relates to synthetic resin compositions. More specifically, this invention relates to synthetic resin compositions excellent in light resistance and heat resistance.

Technical background

10 It has generally been known that molded articles of synthetic resins such as polyvinyl chloride, a polyethylene and an ABS resin, when used out of doors for a long period of time, are affected by sunrays such as ultraviolet rays, heat rays, etc., and a decline in their mechanical strength or a change in their color is
15 caused thereby. In order to prevent these phenomena, there have been used various ultraviolet ray stabilizers of the benzophenone, benzotriazole, benzoate or piperidine series. Out of these ultraviolet ray stabilizers, the compounds having piperidyl groups, i.e. the so-called
20 hindered amine-type ultraviolet ray stabilizers have been universally used for synthetic resins because of their excellent property of stabilizing ultraviolet rays, and there has been extensively made a study of development and application thereof.

25 It has been known, however, that when compounds having piperidyl groups per se are singly blended with synthetic resins as an ultraviolet ray stabilizer, the activity of the piperidyl groups is imparted by substances contained in said resins and detrimental to the piperidyl
30 groups. As the origin of such substances detrimental to the piperidyl groups, there may be mentioned, for example, catalyst residues at the time of polymerization of said resins, various heat stabilizers for imparting heat stability at the time of processing at high temperatures,
35 halogen-containing resins which per se have detrimental halogens, synthetic resins having fire retardants of the halogen series blended therewith, etc.

- 2 -

Compound having piperidyl groups are affected in some way or other by such substances as above contained in synthetic resins and at the time of processing at high temperatures, and there has been observed a decline in the effect of blending.

Disclosure of the invention

It is an object of this invention to provide novel synthetic resin compositions.

It is another object of this invention to provide synthetic resin compositions excellent in light resistance and heat resistance.

It is a further object of this invention to provide novel synthetic resin compositions which can exhibit at its maximum an improvement of light resistance and heat resistance based on compounds having at least one piperidyl group.

The further object and advantages of this invention will be made clear from the below description.

The above objects and advantages of this invention, according to this invention, can be achieved by synthetic resin compositions comprising

(A) 100 parts by weight of a synthetic resin and

(B) 0.01-10 parts by weight of a mixed product of

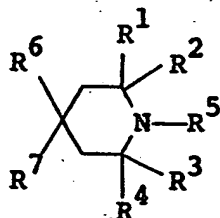
(a) a compound having at least one piperidyl group,

(b) perchloric acid, and

(c) optionally, an inorganic substance other than perchloric acid.

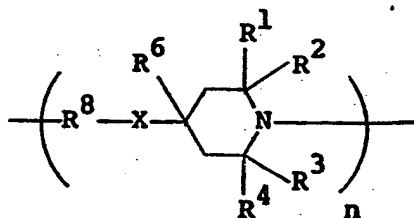
The mixed product (B) used in this invention is a mixed product of (a) a compound having at least one piperidyl group and (b) perchloric acid, or a mixed product of (a), (b) and (c) an inorganic substance other than perchloric acid. As the compound having at least one piperidyl group, there may be mentioned, for example, a compound expressed by the below formula (1):

- 3 -



... (1)

5 wherein R^1 , R^2 , R^3 and R^4 are identical or different and each denote a hydrogen atom or an alkyl group having 1-4 carbon atoms; R^5 denotes a hydrogen atom, an alkyl group having 1-4 carbon atoms, a hydroxy alkyl group having 2-4 carbon atoms or an acyl group having 2-4 carbon atoms; and R^6 and R^7 are identical or different and each denote a monovalent organic group, for example, an acyloxy group and a substituted amino group, or R^6 and R^7 may together form a substituted alkylenedioxy group, or a polymer expressed by the below formula (2):



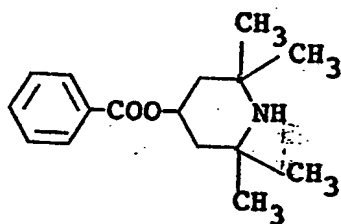
... (2)

15 wherein the definitions of R^1 , R^2 , R^3 , R^4 and R^6 are the same as in the above formula (1); X denotes a group -NH- or -COO-; R^8 denotes a divalent organic group; and n is a number showing a degree of polymerization.

20 As the compounds having piperidyl groups used in this invention, for example, as compounds covered by the above formula (1), there may be mentioned the below compounds:

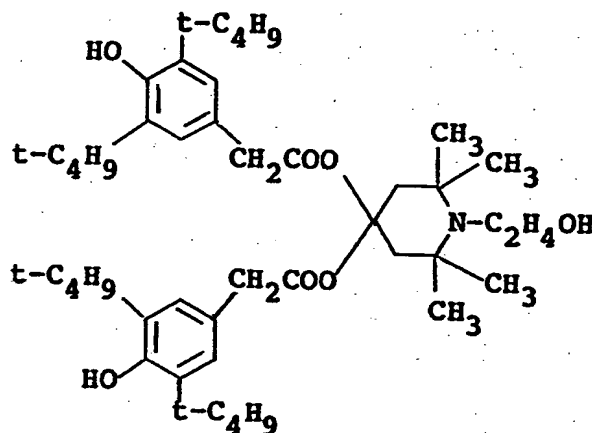
- 4 -

2,2,6,6-tetramethyl-4-piperidylbenzoate:

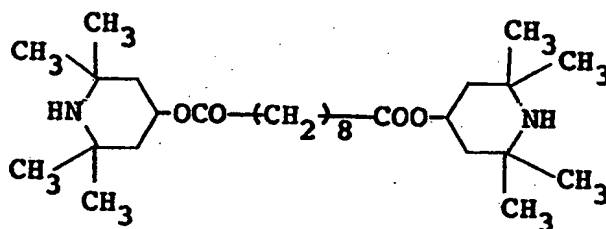


5

N-hydroxyethyl-2,2,6,6-tetramethyl-4-piperidylbis(3,5-di-t-butyl-4-hydroxyphenylpropionate):

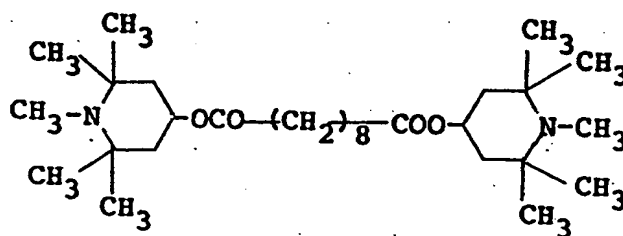


Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate:



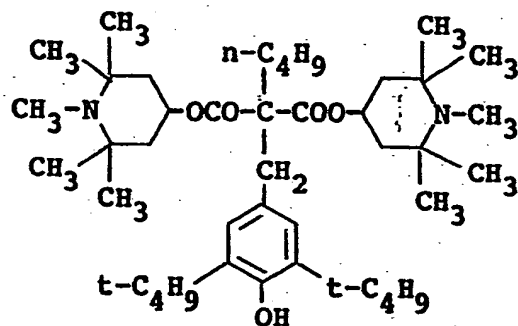
10

Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate:



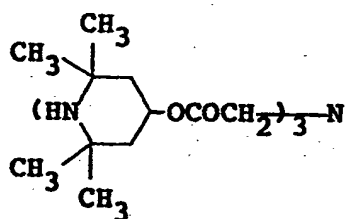
- 5 -

Bis(1,2,2,6,6-pentamethyl-4-piperidyl)-2-n-butyl-2-(3,5-di-t-butyl-4-hydroxybenzyl) malonate:



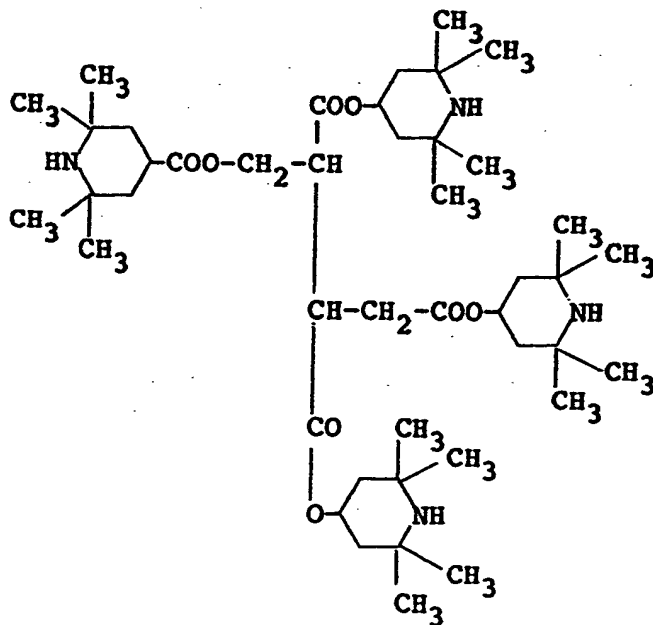
5

Tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate:



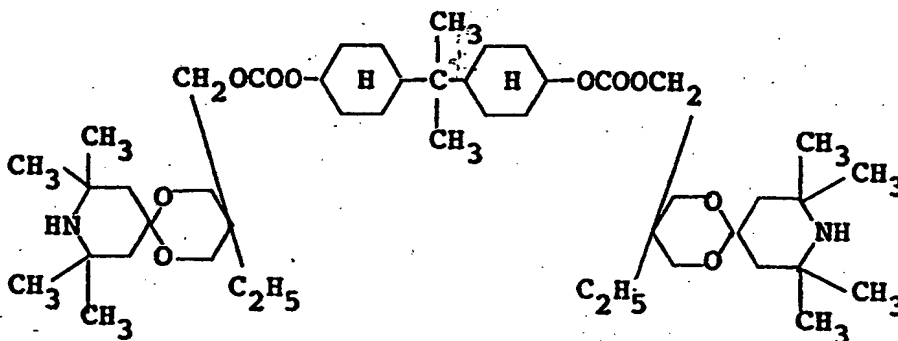
Tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate:

10



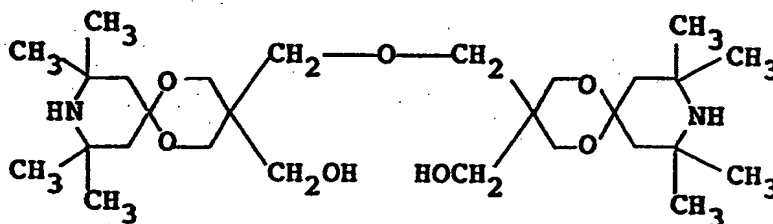
- 6 -

Bis(9-aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro [5,5]-3-undecylmethyloxycarbonyloxy)-4,4'-isopropylidenebiscyclohexane:



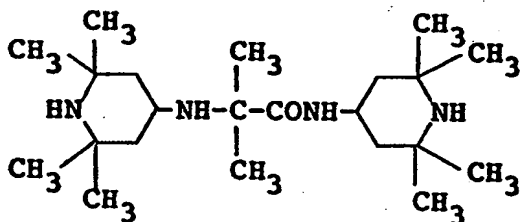
5

Bis(9-aza-8,8,10,10-tetramethyl-3-hydroxymethyl-1,5-dioxaspiro [5,5]-3-undecylmethyl) ether:



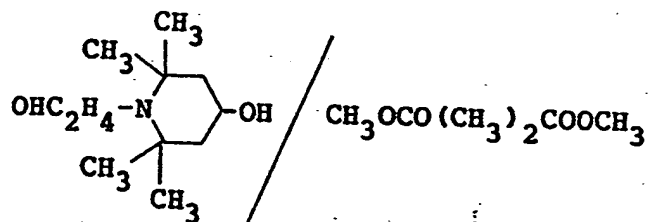
10

[2-[(2,2,6,6-tetramethyl-4-piperidyl)iminol] 2-butyryl[(2,2,6,6-tetramethyl-4-piperidyl)-iminol]:

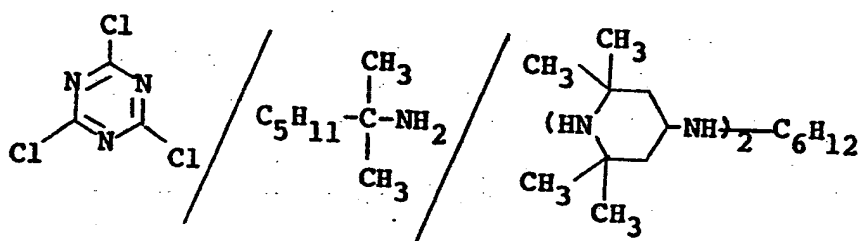


Further, as polymers covered by the above formula (2), there may be mentioned, for example, N-hydroxyethyl-2,2,6,6-tetramethyl-4-piperidynol/dimethyl succinate condensate:

15

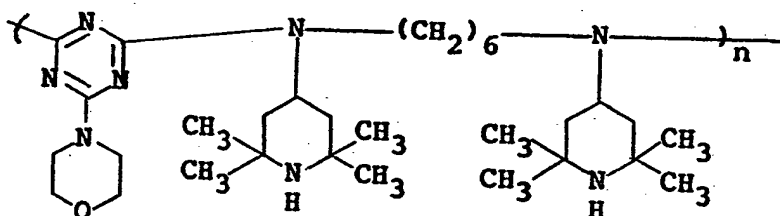


Cyanuric chloride/t-octylamine/bis(2,2,6,6-tetramethyl-4-piperidylamino)hexane condensate:



5

Poly[6-morpholino-1,3,5-triazine-2,4-diyl]-(2,2,6,6-tetramethyl-4-piperidyl)iminohexamethylene[(2,2,6,6-tetramethyl-4-piperidyl-imino)]:



10

As the compounds having piperidyl groups used in this invention, there are preferred compounds expressed by the above formula (1) and having 1-4 piperidyl groups. More preferably, these compounds have a molecular weight of 80-800.

15

The polymers expressed by the above formula (2) have at least n piperidyl groups. n is usually a number of 2-15.

Further, for the mixed product used in this invention, there are used (b) perchloric acid and

optionally an inorganic substance other than perchloric acid.

As the inorganic substance other than perchloric acid, there may be mentioned, for example, an oxide, hydroxide, inorganic acid salt, basic inorganic acid salt or double salt of at least one metal selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, Sn and Pb, further a metallic aluminum powder, or a metal oxide such as SnO_2 , TiO_2 or ZrO_2 .

As the oxide of the metal mentioned in the above group, there may be mentioned, for example, MgO , CaO , BaO , ZnO , SrO_2 , or PbO , and as the hydroxide of said metal, there may be mentioned, for example, LiOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$.

As the inorganic acid which provides an inorganic acid salt or basic inorganic acid salt of a metal, there may be mentioned, for example, phosphoric acid, phosphorous acid, sulfuric acid, sulfurous acid, nitric acid, nitrous acid, carbonic acid, boric acid or silicic acid.

The inorganic acid salt or basic inorganic acid salt can be produced by an ordinary method such as coprecipitation or fusion, for example, from the above-mentioned inorganic acid and metal or an oxide or hydroxide of said metal.

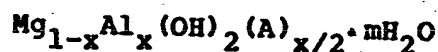
The basic inorganic acid salt may also be an optional mixture of an inorganic acid salt and an oxide or hydroxide.

These salts may also be in the form of a double salt. Further, these salts may also be anhydrides or those having crystal water.

As the inorganic acid salt in the form of an anhydride, there may be mentioned, for example, LiSiO_3 , Na_2SO_4 , Na_2HPO_4 , K_2CO_3 , $\text{Mg}(\text{PO}_4)_2$, $\text{Mg}(\text{NO}_3)_2$, MgCO_3 , CaCO_3 , SrHPO_4 , BaSiO_3 , ZnPO_4 , $\text{Al}_2(\text{HPO}_3)_3$, SnHPO_3 , PbSiO_3 , ZnB_4O_7 or $\text{Ba}(\text{BO}_2)_2$.

As the basic inorganic acid salt in the form of an anhydride, there may be mentioned, for example,
 $2\text{CaO} \cdot \text{Na}_3\text{PO}_4$, $\text{MgO} \cdot \text{K}_2\text{SiO}_3$, $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$, $\text{Al}(\text{OH})_3 \cdot \text{MgSO}_4$,
 $3\text{CaO} \cdot \text{Ca}_3(\text{PO}_4)_2$, $\text{Sr}(\text{OH})_2 \cdot \text{Sr}_3(\text{PO}_4)_2$, $3\text{BaO} \cdot \text{Ba}_2\text{SiO}_3$,
 5 $2\text{ZnO} \cdot \text{ZnHPO}_3$, $\text{Al}_2\text{O}_3 \cdot \text{Al}(\text{PHO}_3)_3$, $3\text{SnO} \cdot \text{Sn}_3(\text{PO}_4)_2$, $3\text{PbO} \cdot \text{PbSO}_4$
 or $5\text{Ca}(\text{OH})_2 \cdot \text{Ca}_2(\text{BO}_3)_2$.

Further, in this invention, as the inorganic salt, there may be used a complex compound of Mg and Al hydroxide having a composition expressed by the below
 10 formula:



wherein x is a number which satisfies $0 < x \leq 0.5$,
 A is CO_3^{2-} or SO_3^{2-} , and m is a number of 0-5,
 which is known as a hydrotalcite compound. A compound
 15 having a composition equivalent to the composition in which in the above compositional formula, part or all of Mg has been substituted with a divalent metal such as Ca, Sr, Ba or Zn can also be used as the inorganic salt.

As the inorganic substance, the above-mentioned
 20 compounds may be used singly or in combination.

The mixed product (B) used in this invention can be prepared by mixing a compound (a) having at least one piperidyl group and perchloric acid (b) and optionally an inorganic substance (c) other than perchloric
 25 acid in an optional order. When the compound (a) and the perchloric acid (b) are used, it is a matter of course to mix these compounds with each other. When the compound (a), the perchloric acid (b) and the inorganic substance (c) are used, there may be mentioned four methods: a
 30 method of first mixing the compound (a) with the inorganic substance (c) and then mixing the mixture with the compound (b); a method of first mixing the compound (a) with the compound (b) and then mixing the mixture with the inorganic substance (c); a method of first

mixing the inorganic substance (c) with the compound (b) and then mixing the mixture with the compound (a); and a method of simultaneously mixing the compound (a), the inorganic substance (c) and the compound (b). Of these methods, the method of first mixing the compound (a) with the inorganic substance (c) and then mixing the mixture with the compound (b) is preferred, because the resulting mixed product is obtained as a comparatively good powdery substance. If the resulting mixed product is in not very good powdery conditions, it is desirable to pulverize the mixed product into a good powdery substance for use.

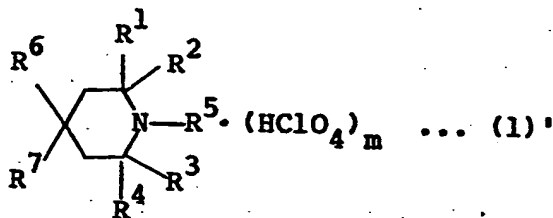
The mixed product used in this invention has an average particle diameter of preferably $100-1\mu\text{m}$, more preferably $10-1\mu\text{m}$.

The ingredients may be mechanically and directly mixed using no medium. They can also be mixed in an inert medium such as an alcohol, for instance.

Proportions in which the compound (a), perchloric acid (b) and inorganic substance (c) are mixed may be 0.05-19 parts by weight each of the perchloric acid (b) and inorganic substance (c) per 1 part by weight of the compound (a), but more preferably 0.1-5 parts by weight of the perchloric acid (b) and 0.1-16 parts by weight of the inorganic substance (c) per 1 part by weight of the compound (a). The most preferable proportions are those within the above-mentioned ranges and in which, for instance, the resulting mixed product has not a pH of 3 or below, i.e. strong acidity.

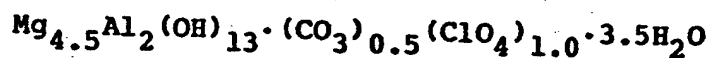
It is not necessarily clear what compound the mixed product (B) used in this invention is. It is believed, however, that when the compound (a) is expressed, for example, by the above formula (1), between the compound (a) and the perchloric acid (b), there is formed an addition compound which is expressed by the below formula (1)':

- 11 -

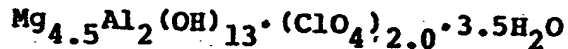


wherein the definitions of R^1 - R^5 are the same as defined in the formula (1), and m is a number of 0.01-1.

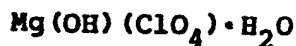
5 Further, it is suggestive, it is believed, that as a compound which is formed among the compound (a), the perchloric acid (b) and the inorganic substance (c), between the perchloric acid (b) and the inorganic substance (c), there is formed a compound expressed by the
10 below formula:



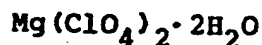
or



in accordance with an amount of the perchloric acid (b)
15 in the case where the inorganic substance (c) is a hydrotalcite group compound having a composition, for example, of $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13} \cdot \text{CO}_3 \cdot 3.5\text{H}_2\text{O}$, or there is formed a compound expressed by the below formula:



20 or



in accordance with an amount of the perchloric acid (b) in the case where the inorganic substance (c) is magnesium hydroxide.

25 As the synthetic resin (A) used in this invention, there may be mentioned, for example, a halogen-containing resin, a polyolefin resin, a copolymer

- 12 -

of an olefin and a vinyl group-containing carboxylic acid or its ester, a styrene resin, a polyester resin, a polyamide resin, a polyacrylonitrile resin, a polymethacrylic resin, a polycarbonate resin, a polyacetal resin, 5 a polyvinyl acetate resin, a polyurethane resin, an epoxy resin, an urea resin, a melamine resin, and a phenol resin.

Of these resins, as the halogen-containing resin, there may be mentioned, for example, polyvinyl 10 chloride, polyvinyl bromide, polyvinyl fluoride, polyvinylidene chloride, chlorinated polyethylene, chlorinated polypropylene, brominated polyethylene, chlorinated rubber, a vinyl chloride/vinyl acetate copolymer, a vinyl chloride/ethylene copolymer, a vinyl chloride/propylene 15 copolymer, a vinyl chloride/styrene copolymer, a vinyl chloride/isobutylene copolymer, a vinyl chloride/vinylidene chloride copolymer, a vinyl chloride/styrene/maleic anhydride terpolymer, a vinyl chloride/styrene/acrylonitrile copolymer, a vinyl chloride/butadiene copolymer, 20 a vinyl chloride/isoprene copolymer, a vinyl chloride/chlorinated propylene copolymer, a vinyl chloride/vinylidene chloride/vinyl acetate terpolymer, a vinyl chloride/acrylate copolymer, a vinyl chloride/maleate copolymer, a vinyl chloride/methacrylate copolymer, 25 a vinyl chloride/acrylonitrile copolymer, a vinyl chloride/urethane copolymer, etc.

As the polyolefin resin, there may be mentioned, for example, polyethylene, polypropylene, polybutylene, polyisobutylene, etc.

30 As the copolymer of an olefin and a vinyl group-containing carboxylic acid or its ester, there may be mentioned, for example, a copolymer of an olefin such as ethylene, propylene, butylene or isobutylene and a vinyl group-containing carboxylic acid or its ester such 35 as vinyl acetate, vinyl propionate, vinyl benzoate, acrylic acid, methacrylic acid, an acrylic ester or methacrylic ester.

- 13 -

As the styrene resin, there may be mentioned, for example, polystyrene, AS, ABS, etc.

As the polyester resin, there may be mentioned, for example, polyethylene terephthalate, polybutylene terephthalate, etc.

Though there have been given no examples of the other synthetic resins, this invention is applied to synthetic resins known to persons skilled in the art.

Further, a blend of synthetic resins, for example, the so-called polymer blend such as a blend of a vinyl chloride resin and an ABS resin or a blend of a vinyl chloride resin and a polyurethane resin is also used as the synthetic resin (A) in this invention.

The synthetic resin compositions of this invention contain 0.01-10 parts by weight of the mixed product (B) in this invention per 100 parts by weight of the synthetic resin (A). If the amount of said mixed product is below the lower limit, said mixed product will have little effect. If the amount of said mixed product exceeds the upper limit, no effect can be expected from the increased amount, and this is useless from the economical point of view. Preferably, said mixed product is contained in an amount of 0.1-3 parts by weight based on the same as above.

The synthetic resin is blended with a fire retardant for the purpose of making the resin fire retardant. The compositions of this invention also exhibit an improvement effect in the case where there is blended a fire retardant, especially a retardant of the halogen series.

The compositions of this invention containing a fire retardant, for example, a fire retardant of the halogen series exhibit more excellent stability to ultraviolet rays and more excellent fire retardancy than known resin compositions containing an ultraviolet stabilizer having piperidyl groups and a fire retardant of the halogen series.

As the fire retardant of the halogen series which is used for the composition of this invention, there may be mentioned, for example, halogen-containing phosphoric esters, aliphatic chlorides, aliphatic bromides, aromatic chlorides, aromatic bromides, etc., i.e. halogen-containing phosphoric esters such as tris-chloroethyl phosphate, tris(dichloropropyl) phosphate, trischloropropyl phosphate, tris-dichloropropyl chloropropyl phosphate, bischloropropyl dichloropropyl phosphate, bischloropropyl chloroethyl phosphate, bischloroethyl dichloropropyl phosphate, tris(dibromopropyl) phosphate and tris(bromochloropropyl) phosphate; and chlorides or bromides of aliphatic or aromatic hydrocarbons such as acetylene tetrabromide, dibromotetra-
chloroethane, tetrabromoethane, tetrabromobutane, acetic
acid dibromide, ethylbenzene pentabromide, benzene
tetrabromide, benzene pentabromide, benzene hexabromide,
pentabromo-cyclohexane chloride, ethane hexachloride,
methane diiodide, ammonium bromide, brominated poly-
phenyl, chlorinated polyphenyl, perchloropentacyclo-
decane, 1,2-dibromo-3-chloropropane, 1,2,3-tribromo-
propane, hexabromocyclododecane, chlorinated diphenyl,
chlorotetrabromoethane, tetrabromobisphenol A, tetra-
bromophthalic anhydride, hexabromocyclododecane, bis-
(bromoethylether)tetrabromobisphenol A, tetrachloro-
phthalic anhydride, chlorendic acid, chlorentic acid,
chlorinated paraffin, tribromopolystyrene and deca-
bromodiphenoxyethane.

The compositions of this invention exhibit especially excellent light resistance and heat resistance in the case where the synthetic resin (A) is a halogen-containing resin and/or contains a fire retardant of the halogen series.

Further, for the compositions of this invention, there may be used one or more types of common additive according to types of the synthetic resin. As

- 15 -

such additives, there may be mentioned, for example, antioxidants, organic phosphite compounds, ultraviolet stabilizers, metal salts of organic acids, oxides of metals, hydroxides of metals, basic salts of inorganic acids, hydrotalcite compounds, metal salts of organic phosphoric acid, polyols, nitrogen-containing non-metallic compounds, beta-diketone compounds, epoxy compounds, organic tin compounds, etc.

Of these common additives, metal salts of organic acids and organic phosphite compounds have the effect of further improving the properties of the compositions of this invention.

As such organic acids, for example, carboxylic acids or phenols are preferred, and as the salts thereof, for example, salts of Li, Na, K, Mg, Ca, Sr, Ba, Cd, Pb and Sn are preferred. As such carboxylic acids, there may be mentioned, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, 2-ethylhexoic acid, tridecanoic acid, capric acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, 12-hydroxystearic acid, oleic acid, linoleic acid, linolenic acid, thioglycolic acid, mercaptopropionic acid, laurylmercaptpropionic acid, benzoic acid, p-t-butylbenzoic acid, dimethylbenzoic acid, aminobenzoic acid, salicylic acid, amino acid, glutamic acid, oxalic acid, glutaric acid, succinic acid, malonic acid, adipic acid, phthalic acid, fumaric acid, maleic acid, malic acid, citric acid, tartaric acid, thiodipropionic acid, trimellitic acid, pyromellitic acid, mellitic acid, etc.

As examples of the phenols, there may be mentioned phenol, nonylphenol, t-butylphenol, octylphenol, isoamylphenol, cresol, xylate, etc.

As examples of preferred organic phosphite compounds, there may be mentioned isooctylphosphite, distearylphosphite, triisodecylphosphite, triisooctyl-

phosphite, trilaurylphosphite, tristearylphosphite, tridipropyleneglycolphosphite, diphenylphosphite, tri-isononylphenylphosphite, triphenylphosphite, diphenylisodecylphosphite, diphenylisooctylphosphite, phenyl-
5 diisooctylphosphite, diisodecylpentaerythritoldi-phosphite, tetraphenyldipropyleneglycoldiphosphite, polydipropyleneglycolphenylphosphite, trilauryltri-thiophosphite, trisnonylphenylphosphite, distearyl-pentaerythritoldiphosphite, bis(2,4-di-t-butylphenyl)-
10 pentaerythritoldiphosphite, dilaurylphosphite, ditridecylphosphite, ethylhexyldiphenylphosphite, phenyl-neopentyleneglycolphosphite, heptakistripropyleneglycol-phosphite, diphenyldidecyl(2,2,4-trimethyl-1,3-penta-
diol)diphosphite, diisooctylphenylphosphite, poly-
15 4,4'-isopropylidenephphenolneodol 25 alcohol phosphite, etc. Further, fire retardant aids such as antimony trioxide and inorganic borates, plasticizers, lubricants, pigments, foaming agents, fillers, antistatic agents, heavy metal-inactivating agents, nucleating agents,
20 processing aids, etc. may be added, as required, to the compositions of this invention.

With reference to examples, this invention will be more specifically described below.

Table 1 below shows mixed products used in
25 Examples 1-16 and compounds having piperidyl groups used for the production thereof.

Table 1

Compound having piperidyl group		Mixed product		
Compound	abb.	Amount of compound used		abb.
		Piperidyl compound	Perchloric acid (in terms of 100 % perchloric acid)	
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	a	481 g	200 g	A
do.	a	481	100	B
2-[(2,2,6,6-tetramethyl-4-piperidyl)iminol-2-buteryl[(2,2,6,6-tetramethyl-4-piperidyl)imino]	c	381	200	C
Bis(1,2,2,6,6-pentamethyl-4-piperidyl)-2-n-butyl-2-(3,5-di-t-butyl-4-hydroxybenzyl)-malonate	d	685	200	D
Cyanuric chloride/t-octylamine/bis(2,2,6,6-tetramethyl-4-piperidylamino)hexane condensate	e	250	20	E
Poly[6-morpholino-1,3,5-triazine-2,4-diyl]-(2,2,6,6-tetramethyl-4-piperidyl)iminohexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]	f	150	54	F

- 18 -

The mixed products were prepared as below.

Preparation of mixed products A, B and D:

Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (a) (481 g) was dissolved in 200 g of methanol, and 334 g of an aqueous solution of 60 % perchloric acid (200 g in terms of 100 % perchloric acid) was dropwise added thereto with stirring. After the dropwise addition, the stirring was continued for 1 hour, and the solvent was evaporated to give a white-colored powdery product (A) having a melting point of 140-150 °C.

In the same way as above, mixed products B and D were prepared respectively using compounds b and d as compounds having piperidyl groups.

Preparation of mixed products E, F and C:

An aqueous solution of 20 % perchloric acid (100 g) (20 g in terms of 100 % perchloric acid) was dropwise added with stirring to 250 g of a cyanuric chloride/t-octylamino/bis(2,2,6,6-tetramethyl-4-piperidylamino)hexane condensate (e). After the dropwise addition, the stirring was continued for about 1 hour, and drying was carried out under reduced pressure to give a white-colored powder (E) having a melting point of 135-160 °C.

In the same way as above, mixed products F and C were prepared respectively using compounds f and c as compounds having piperidyl groups.

EXAMPLES 1-4 and COMPARATIVE EXAMPLES 1-3

In each run, test sheets having a thickness of 0.5 mm were prepared by means of a kneading roll using a blend of the below formulation:

	Polyvinyl chloride	100 parts by weight (halogen resin)
	DOP	40 do.
	Epoxidized soybean oil	1.0 do.
	TiO ₂	1.0 do.
35	Ba-nonylphenate	0.8 do.
	Zn-stearate	0.2 do.
	Mixed product	0.2 do.

- 19 -

The test sheets were examined for discoloration under the conditions of 180 °C, 15 minutes and 30 minutes using a Geer oven, and a degree of discoloration was visually judged. Further, a degradation by light was measured using a sunshine weatherometer. A degree of degradation was expressed by a retention of elongation (%) after an elapse of 400 hours. Furthermore, the degree of discoloration of the test sheets after an elapse of the same period of time as above was visually observed, and a color tone was also described. It is shown that the closer the retention of elongation is to 100 %, the less the degradation by light is. For comparison, the same tests were conducted on a blend of the same formulation except that 0.2 part by weight of a compound having piperidyl groups was used instead of 0.2 part by weight of the mixed product. The results are shown in Table 2.

- 20 -

Table 2

	Run No.	Mixed product or compound having piperidyl group	Discoloration at 180 °C		Sunshine weatherometer (400 hours)	
			15 min.	30 min.	Retention of elongation (%)	Color of test piece
Example	1	A	white	pale yellow	95	pale yellow
	2	B	white	pale yellow	90	pale yellow
	3	D	white	pale yellow	95	pale yellow
	4	E	white	pale yellow	90	pale yellow
Comparative Example	1	a	pale brown	brown	66	brown
	2	d	pale brown	brown	72	brown
	3	e	pale brown	brown	61	brown

EXAMPLES 5-6 and COMPARATIVE EXAMPLES 4-5

In each run, test sheets having a thickness of 0.5 mm were prepared by kneading and then pressing a blend of the below formulation:

Polyethylene	100 parts by weight (non-halogen resin)
Perchloropentacyclodecane	15 do. (fire retardant of the halogen series)
Ca stearate	1.0 do.
Pentaerythrityl-tetrakis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate	0.2 do.
Distearylthiodipropionate	0.1 do.
Mixed product	0.2 do.

A period of time till the test sheets brittled (light resistance) was measured using a sunshine weatherometer. Further, a degree of discoloration after an elapse of 500 hours was measured. The results are shown in Table 3.

Table 3

		Mixed product or compound having piperidyl group	Sunshine weatherometer	
			Light resistance (hours)	Degree of discoloration after an elapse of 500 hrs.
Example	5	C	1030	pale yellow
	6	F	1150	pale yellow
Comparative Example	4	c	750	pale brown
	5	f	870	pale brown

In Comparative Examples 4 and 5, there was used a blend of the same formulation as in Example 5 except that 0.2 part by weight of the mentioned compound having piperidyl groups was used instead of 0.2 part by weight of the mixed product.

EXAMPLES 7-9 and COMPARATIVE EXAMPLES 6-7

In each run, test sheets having a thickness of 0.5 mm were prepared by kneading and then pressing a blend of the below formulation:

- 22 -

	Polypropylene	100 parts by weight (non-halogen resin)
	Tribromopolystyrene	10 do. (fire retardant of the halogen series)
	Ca stearate	0.3 do.
	Pentaerythrityl-tetra- kis[3-(3,5-di-t-butyl-4- hydroxyphenyl)propionate	0.2 do.
5	Mixed product	0.3 do.

A period of time till the test sheets brittled (light resistance) was measured using a fadeometer. The results are shown in Table 4.

For comparison, the same tests were conducted on a blend of the same formulation as above except that 0.3 part by weight of a compound having piperidyl groups was used instead of 0.3 part by weight of the mixed product.

Table 4

		Mixed product or compound having piperidyl group	Light resistance measured by means of a fedeometer (hours)
Example	7	A	610
	8	D	650
	9	E	720
Compara- tive Example	6	a	450
	7	e	510

EXAMPLES 10-12 and COMPARATIVE EXAMPLES 8-9

In each run, test sheets having a thickness of 2 mm were prepared by kneading and then pressing a blend of the below formulation:

- 23 -

ABS resin 100 parts by weight
 (non-halogen resin)
 Tetrabromobisphenol A 9 do.
 (fire retardant of
 the halogen series)
 4,4'-butyridenebis-
 (3-methyl-6-t-butyl-
 phenol) 0.1 do.
 Mixed product 0.2 do.

5 A retention of tensile strength of the test
 sheets after an elapse of 500 hours in a weatherometer
 was measured. For comparison, the same tests as above
 were conducted on a blend of the same formulation as
 above except that 0.2 part by weight of a compound having
 10 piperidyl groups was used instead of 0.2 part by weight
 of the mixed product.

The results are shown in Table 5.

Table 5

Run No.		Mixed product or compound having piperidyl group	Retention of tensile strength (%)
Example	10	C	81
	11	D	80
	12	F	85
Comparative Example	8	c	55
	9	f	63

15

EXAMPLES 13-16

In each run, test sheets having a thickness of
 0.5 mm were prepared by kneading a blend of the below
 formulation at a temperature of 180 °C using a kneading
 roll. A retention of elongation and a degree of dis-
 20 coloration after an elapse of 1000 hours were measured
 using a sunshine weatherometer.

5	Polyvinyl chloride	70 parts by weight (halogen resin)
	ABS resin	30 do. (non-halogen resin)
	Trisdibromopropyl phosphate	0.2 do. (fire retardant of the halogen series)
	DOP	30 do.
	Calcium carbonate	10 do.
	Ba-stearate	1.0 do.
	Zn-octoate	0.5 do.
	ST-210*1	0.5 do.
	Mixed product C	0.3 do.
	Organic phosphite compound	mentioned in Table 6

*1 A partial ester of dipentaerythritol di-
basic acid, a product of Ajinomoto K. K.
The results are shown in Table 6.

Table 6

Example No.	Organic phosphite compound		Sunshine weatherometer (1000 hours)	
	Type	Amount added (part by weight)	Retention of elon- gation (%)	Color of test piece
13	Diphenyldecyl phosphite	0.8	70	pale yellow
14	Tetra(tridecyl)- 4,4'-isopropylidene- diphenyldiphosphite	0.4	65	pale yellow
15	Trisnonylphenyl- phosphite	0.4	60	pale yellow
16	Distearylentaery- thritoldiphosphite	0.2	63	pale yellow

The mixed products used in Examples 17-44 were prepared as follows using the compound having piperidyl groups mentioned in Table 1.

Preparation of mixed product G:

- 5 The compound a mentioned in Table 1 (481 g) as the compound having piperidyl groups and 507 g of a hydrotalcite compound $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$ (trade name: DHT-4A, a product of Kyowa Chemical Industry Co., Ltd.), as an inorganic substance were mixed with each
10 other for 5 minutes by means of a high-speed Henschel mixer to give 985 g of a mixture (hereinafter referred to as a preparatory mixture).

- 15 The preparatory mixture (985 g) and 500 g of methanol were stirred by means of a universal stirrer for a powdery substance into a slurry. Perchloric acid (361 g) was dropwise added to the slurry with stirring. After the dropwise addition, the stirring was continued for 1 hour. The solvent was evaporated, and the residue was pulverized to give a white-colored powdery product G.

- 20 Preparation of mixture product H:

- 25 A preparatory mixture (985 g) prepared in the same formulation as in case of the mixed product G was put in a universal stirrer for a powdery substance and stirred in a state of powdery substance. Perchloric acid (120 g) was dropwise added thereto with stirring. After one hour of the stirring, the mixture was dried under reduced pressure and pulverized to give a white-colored powdery product H.

Preparation of mixed product M:

- 30 The compound f mentioned in Table 1 (1500 g) as a compound having piperidyl groups and 420 g of MgCO_3 and 405 g of $\text{Ca}_3(\text{PO}_4)_3$ as inorganic substances were mixed with each other for 5 minutes by means of a high-speed Henschel mixer to give 2320 g of a preparatory mixture.

- 35 The preparatory mixture (2320 g) and 1000 g of methanol were stirred by means of a universal stirrer for

a powdery substance to give a slurry. Perchloric acid (1500 g) was dropwise added bit by bit to the slurry with stirring. When 1500 g of the perchloric acid was dropwise added, the slurry showed a pH of 6.8, and so the dropwise addition of the perchloric acid was terminated. The stirring was further continued for 1 hour. The solvent was evaporated, and the residue was pulverized to give a white-colored powdery product M.

Preparation of mixed product N:

10 A preparatory mixture (2320 g) prepared in the same formulation as in case of the mixed product M was put in a universal stirrer for a powdery substance, and 700 g of perchloric acid was dropwise added thereto. Stirring was carried out for 1 hour. Then, the mixture
15 was dried under reduced pressure and pulverized to give a white-colored powdery product N.

 Mixed products I, J, K and L were prepared in the formulations mentioned in Table 7 below in the same way as in case of the mixed products G, H, M and N. In
20 Table 7, there was also mentioned the formulation each of the mixed products G, H, M and N.

- 27 -
Table 7

Mixed product	Compounds having piperidyl group		Inorganic substance		Per-chloric acid
	abb.	Amount used	Compound	Amount used	Amount used
G	a	481 g	DHT-4A	507 g	361 g
H	"	"	"	"	120 g
I	c	381	Alcamizer-4* SiO ₂	270 100	150 g
J	"	"	Ca(OH) ₂ Al powder	110 9	240 g
K	d	685	Ba(OH) ₂ ·BaSO ₄	202	210 g
L	e	250	DHT-4A 3SnO·Sn ₃ (PO ₄) ₂	507 158	250 g
M	f	150	MgCO ₃ Ca ₃ (PO ₄) ₃	42 41	150 g
N	"	150	MgCO ₃ Ca ₃ (PO ₄) ₃	42 41	70 g

* Alcamizer-4, the trade name of a product of Kyowa Chemical Industry Co., Ltd. (a hydro-talcite compound in which part of Mg is substituted with Zn)

- 28 -

EXAMPLES 17-23 and COMPARATIVE EXAMPLES

In each run, test sheets having a thickness of 0.5 mm were prepared by means of a kneading roll using a blend of the below formulation:

5	Polyvinyl chloride	100 parts by weight
	DOP	40 do.
	Epoxidized soybean oil	2.0 do.
	TiO ₂	0.5 do.
	Ba-nonylphenate	0.7 do.
10	Zn-stearate	0.3 do.
	Mixed product	mentioned in Table 8
	mentioned in Table 8	

The test sheets were examined for discoloration under the conditions of 180 °C, 15 minutes and 30 minutes using a Gear oven, and a degree of discoloration was visually judged. Degradation by light was measured using a sunshine weatherometer. A degree of degradation was expressed by a retention of elongation (%) after an elapse of 800 hours. The degree of discoloration of the test sheets after an elapse of the same period of time was visually observed, and a color tone has also been described. It is shown that the closer the retention of elongation is to 100 %, the less the degradation by light is. For comparison, the same tests as above were conducted on preparatory mixtures corresponding to the mixed products prior to preparation with perchloric acid. The results are shown in Table 8.

In Table 8, G-N in the column of types of mixed products respectively denote the mixed products mentioned in Table 7, G'-N' denote corresponding preparatory mixtures (mixed products of a compound having piperidyl groups and an inorganic substance; The same applies to the following.), and a denotes the compound having piperidyl groups mentioned in Table 1.

- 29 -
Table 8

Run No.		Mixed product		Discoloration at 180 °C		Sunshine weatherometer (800 hours)	
		Type	Amount of the product used	15 min.	30 min.	Retention of elongation (%)	Color of test piece
Example	17	G	0.2	white	pale yellow	90	pale yellow
	18	H	0.2	"	"	87	"
	19	I	0.2	"	"	90	"
	20	J	0.2	"	"	85	"
	21	K	0.2	"	"	83	"
	22	L	0.2	"	"	92	"
	23	M	0.2	"	"	90	"
	24	N	0.2	"	"	85	"
Comparative Example	10	G'	0.2	pale yellow.	brown	65	brown
	11	H'	0.2	"	"	60	"
	12	I'	0.2	"	"	67	"
	13	J'	0.2	"	"	60	"
	14	K'	0.2	"	"	65	"
	15	L'	0.2	"	"	73	"
	16	M'	0.2	"	"	65	"
	17	N'	0.2	"	"	60	"
	18	a	0.1	"	"	58	"
	19	a	0.2	"	"	75	"

- 30 -

EXAMPLES 24-27 and COMPARATIVE EXAMPLES 20-23

In each run, test pieces were prepared by extrusion molding using a blend of the below formulation:

5	Polyethylene	100 parts by weight
	Ca stearate	1.0 do.
	Pentaerythrityl-tetra- kis[3-(3,5-di-t-butyl-4- hydroxyphenyl) propionate	0.2 do.
	Dilaurylthiodipropionate	0.1 do.
	Mixed product	0.2 do.

A period of time till the test pieces brittled (light resistance) was measured using a sunshine weatherometer. A degree of discoloration after an elapse of 800 hours was measured. The results are shown in Table 9. For comparison, the same tests as above were conducted on preparatory mixtures, and the results are also shown in Table 9.

Table 9

Run No.		Mixed product	Sunshine weatherometer	
			Light resistance (hours)	Degree of discoloration after an elapse of 800 hrs.
Example	24	G	1600	white
	25	I	1500	white
	26	K	1650	white
	27	M	1450	white
Comparative Example	20	G'	1100	pale yellow
	21	I'	1000	pale yellow
	22	K'	1100	pale yellow
	23	M'	900	pale yellow

- 31 -

EXAMPLES 28-31 and COMPARATIVE EXAMPLES 24-31

In each run, test sheets having a thickness of 0.5 mm were prepared by kneading and then press molding using a blend of the below formula:

5	Polypropylene	100 parts by weight
	Ca stearate	0.5 do.
	Pentaerythrityl-tetra- kis[3-(3,5-di-t-butyl-4- hydroxyphenyl) propionate	0.3 do.
	Mixed product (in Table 10)	Mentioned in Table 10

10 A period of time till the test sheets brittled
(light resistance) was measured using a fadeometer. The
results are shown in Table 10. For comparison, the same
tests as above were conducted on preparatory mixtures
respectively corresponding to the mixed products and
compounds having piperidyl groups. The results are also
15 shown in Table 10.

- 32 -
Table 10

Run No.		Mixed product		Light resistance measured by means of a fadeometer (hours)
		Type	Amount of product used	
Example	28	H	0.2	1100
	29	J	0.2	1200
	30	L	0.2	1000
	31	N	0.2	1100
Comparative Example	24	H'	0.2	500
	25	J'	0.2	550
	26	L'	0.2	400
	27	N'	0.2	550
	28	c	0.1	550
	29	f	0.1	600
	30	c	0.2	850
	31	f	0.2	900

EXAMPLES 32-37 and COMPARATIVE EXAMPLES 32-37

In each run, test press pieces were prepared
5 using a blend of the below formulation containing a fire
retardant:

10	Polypropylene	100 parts by weight
	Fire retardant of the halogen series (types in Table 11)	10 do.
	Ca stearate	1.0 do.
	Diethyl Sn maleate	1.0 do.
	Pentaerythrityl-tetra- kis[3-(3,5-di-t-butyl-4- hydroxyphenyl) propionate	0.2 do.
	Mixed product (in Table 11)	0.3 do.

A period of time till the test pieces brittle (light resistance) was measured using a fadeometer. The results are shown in Table 11.

Table 11

Run No.		Fire retardant	Mixed product	Light resistance measured by means of a fadeometer (hours)
Example	32	perchloropentacyclodecane	G	800
	33	"	J	850
	34	"	L	700
Comparative Example	32	"	G'	450
	33	"	J'	500
	34	"	L'	400
Example	35	tribromopoly-styrene	G	900
	36	"	J	920
	37	"	L	850
Comparative Example	35	"	G'	500
	36	"	J'	550
	37	"	L'	450

EXAMPLES 38-40 and COMPARATIVE EXAMPLES 38-40

In each run, test sheets having a thickness of 2 mm were prepared by kneading and then press molding using a blend of the below formulation:

10	ABS resin	100 parts by weight
	4,4'-butylidenebis(3-methyl-6-t-butylphenol)	0.2 do.
	Mixed product	0.3 do.

A retention of tensile strength after an elapse of 1000 hours was measured using a weatherometer. The results are shown in Table 12. For comparison, the same tests as above were conducted on preparatory mixtures. 5 The results are also mentioned in Table 12.

Table 12

Run No.		Measured prduct	Retention of tensile strength (%)
Example	38	G	85
	39	I	80
	40	K	83
Comparative Example	38	G'	50
	39	I'	40
	40	K'	45

EXAMPLES 41-44

10 In each run, when the mixed product having an average particle diameter of $35\mu\text{m}$ in this invention was further finely pulverized into a mixed product having an average particle diameter of $10\mu\text{m}$ or less, there was given a further improved effect.

15 Test sheets having a thickness of 0.5 mm were prepared by means of a kneading roll using a blend of the below formulation:

- 35 -

	Polyvinyl chloride	70 parts by weight
	ABS resin	30 do.
	Trisbromopropylphosphate (fire retardant of the halogen series)	0.3 do.
	Sb ₂ O ₃ (fire retardant aid)	1.0 do.
5	DOP	40 do.
	Calcium carbonate	10 do.
	Ba nonylphenate	1.0 do.
	Zn octate	0.5 do.
	ST-210*	0.5 do.
10	Mixed product (in Table 13)	0.4 do.

* A partial ester of dipentaerythritol dibasic acid, a product of Ajinomoto K. K.

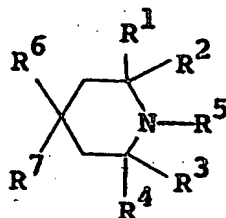
A retention of elongation after an elapse of 1000 hours and a degree of discoloration were measured using a sunshine weatherometer. The results are shown in Table 13.

Table 13

Example	Mixed product		Sunshine weatherometer (1000 hours)	
	Type	Average particle diameter	Retention of elon- gation (%)	Color of test piece
41	I	9 μ m	70	pale yellow
42	M	7 μ m	75	pale yellow
43	I	35 μ m	53	yellow
44	M	35 μ m	60	yellow

SCOPE OF CLAIM

1. A synthetic resin composition comprising
 - (A) 100 parts by weight of a synthetic resin
 - and
 - (B) 0.01-10 parts by weight of a mixed product
 - (a) a compound having at least one piperidyl group,
 - (b) perchloric acid, and
 - (c) optionally, an inorganic substance other than perchloric acid.
2. The composition of claim 1 wherein the synthetic resin (A) is a halogen-containing resin.
3. The composition of claim 1 wherein the synthetic resin (A) is a polyolefin resin or a styrene resin.
4. The composition of claim 1 wherein the synthetic resin (A) is a mixture of a halogen-containing resin and a polyolefin resin or a styrene resin.
5. The composition of claim 1 wherein the compound having at least one piperidyl group is a compound having 1-4 piperidyl groups in the molecule.
6. The composition of claim 1 wherein the compound having at least one piperidyl group is expressed by the below formula (1):



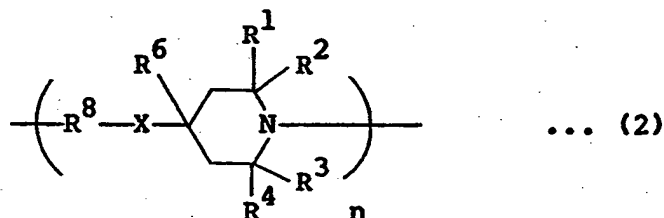
... (1)

wherein R^1 , R^2 , R^3 and R^4 are identical or different and each denote a hydrogen atom or an alkyl group having 1-4 carbon atoms; R^5 denotes a hydrogen atom, an alkyl group having 1-4 carbon

- 37 -

atoms, a hydroxyalkyl group having 2-4 carbon atoms or an acyl group having 2-4 carbon atoms; and R^6 and R^7 are identical or different and each denote a monovalent organic group, for example, an acyloxy group and a substituted amino group, or R^6 and R^7 may together form a substituted alkylenedioxy group.

7. The composition of claim 1 wherein the compound having at least one piperidyl group is expressed by the below formula (2):



wherein the definitions of R^1 , R^2 , R^3 , R^4 and R^6 are the same as in the above formula (1); X denotes a group -NH- or -COO-; R^8 denotes a divalent organic group; and n is a number showing a degree of polymerization.

8. The composition of claim 1 wherein the inorganic substance is a hydrotalcite compound.
9. The composition of claim 1 wherein the inorganic substance is an oxide, hydroxide, inorganic acid salt or basic inorganic acid salt of a metal selected from the group consisting of Li, Na, K, Mg, Ca, Ba, Zn, Al, Sn and Pb.
10. The composition of claim 1 wherein the inorganic substance is Al, SiO_2 , TiO_2 or ZrO_2 .
11. The composition of claim 1 wherein the mixed product (B) is a mixed product of 1 part by weight of the compound (a), 0.05-19 parts by weight of the inorganic substance (b) and 0.05-19 parts by weight of the perchloric acid (c).

- 38 -

12. The composition of claim 1 wherein the mixed product (B) is a powdery substance having an average particle diameter of 100-1 μ m.

13. The composition of claim 1 containing a fire retardant.

14. The composition of claim 1 containing as a fire retardant a fire retardant of the halogen series.

15. The composition of claim 1 further containing a fire retardant of the halogen series.

INTERNATIONAL SEARCH REPORT

0344321

International Application No

PCT/JP88/01067

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl ⁴ C08K5/34, C08K5/04, C08K3/00, C08L101/00, C07D211/44, C07D211/58		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C08K5/34, C08K5/04, C08K3/00, C08L101/00, C07D211/44, C07D211/58	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
Jitsuyo Shinan Koho 1926 - 1981 Kokai Jitsuyo Shinan Koho 1971 - 1981		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB, A, 1077011 (GILL, JENNINGS & EVERY) 26 July 1967 (26. 07. 67) Page 4, lines 14 to 98 and page 5, lines 5 to 28 (Family: none)	1
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
December 5, 1988 (05. 12. 88)		December 19, 1988 (19. 12. 88)
International Searching Authority		Signature of Authorized Officer
Japanese Patent Office		

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (COPY)

THIS PAGE BLANK (USPTO)